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CIRCULAR No. 466 MARCH 1938
UNITED STATES DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

A WEATHER-RESISTANT FIREPROOFING TREATMENT[1] FOR COTTON FABRICS

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INTRODUCTION

The need for a weather-resistant fireproofing treatment for cotton fabrics has long been recognized, and numerous attempts to develop such a treatment have been made both in this country and abroad. This need is constantly growing, because of the increased use of cotton fabrics in awnings, paulins, tents, brattice cloth, and covers for haycocks and haystacks, trucks, wagons, fire blankets, and airplane wings. No figures are available showing the total loss in goods and lives that occurs through lack of fire resistance of these articles, but it is estimated that this lack costs many millions of dollars annually as well as many lives. A significant hint of the seriousness of lack of fire resistance is given in the fact that the fire regulations of a number of cities prohibit the use on office buildings and apartment houses of awnings that are not fireproof.

There is a difference between the terms "fireproof" and "flameproof" as used in this circular. Although fireproof fabric is charred when heated to the ignition temperature (or even below) for a sufficient time, flame is not propagated into uncharred area, and the fabric does not glow persistently after the igniting flame is removed. Flameproof fabric is also charred under like treatment, and no flame is propagated, but the fabric continues to glow after the igniting flame is removed. This glow persists and slowly spreads over the portion uncharred by the igniting flame, leaving a more or less carbon-free ash.

[1] Covered by U. S. Patents 1961108, 1990292, 2012686, and 2017805, all of which are dedicated to the public.

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The term "weather-resistant" implies that a fireproofing treatment cannot be leached out or otherwise rendered ineffective by the rain, varying temperature, and sunlight. Preferably such a treatment does not shorten the useful life of fabric, but this feature is not directly related to weather resistance.

During the progress of this work in the Bureau of Chemistry and Soils, from 1930 to 1934, samples of all known commercial fireproofed cotton fabrics were carefully tested, but none was found to be entirely satisfactory. Also, a small number of the numerous materials and processes for fireproofing that have been suggested or patented were tested. No effort was made to include them all.

After careful consideration of the numerous materials that have been used for the fireproofing of fabrics, various preliminary trials were made, some of which are referred to later in this circular. In the absence of a simple and highly durable waterproof treatment to prevent the removal of soluble fireproofing materials, it was decided that a modification of the Perkin process, in which stannic oxide is used as the basic weather-resistant flameproofing constituent, held the greatest promise of success. Previous work had shown that to obtain a glowproof or fireproof treatment with this process, it is necessary to use a water-insoluble and weather-resistant material in addition to the stannic oxide. Accordingly, investigations to perfect and make available such a modification were started.

Untreated, unbleached fabric heated to the ignition point over a small area continues to flame when the igniting flame is removed, and if the flame is extinguished an afterglow remains and spreads a considerable distance over the uncharred fabric. During the course of this work it was observed that this afterglow appears to be induced largely by the natural ash of the fabric, and generally is absent from bleached fabric containing a low percentage of ash.

REVIEW OF LITERATURE

Numerous articles have been written on fireproofing, and a large number of patents have been issued in this field. Ramsbottom and Snoad (*9*)[2] have compiled a comprehensive bibliography and list of patents on this subject. Only publications that appear to have a direct bearing on the work described in this circular will be referred to here.

Although much work has been done on the subject, the number of published works which have materially contributed to the knowledge of fireproofing is very limited. The first comprehensive study reported was that of Gay-Lussac (*4*). Although he confined his investigation to water-soluble fireproofing salts, his observations led him to set forth principles of fireproofing which are still accepted. The neglect of these principles has needlessly crowded the patent literature dealing with fireproofing.

Lochtin (*7*) made a study of both water-soluble and water-insoluble compounds of many types. He found only one insoluble compound that possessed fireproofing properties. He did not try stannic oxide. He reported that aluminum hydroxide precipitated from the sulphate

[2] Italic numbers in parentheses refer to Literature Cited, p. 17.

by ammonia possessed no fireproofing qualities, whereas when precipitated from sodium aluminate by carbon dioxide or a carbonate it was satisfactory as a fireproofing material.

Ramsbottom and Snoad (*9*) have made one of the most fundamental and important studies of the fireproofing problem. However, they concentrated their attention chiefly on a study of borax-boric acid mixtures and devoted only a small portion of their investigation to materials which have weather resistance, including stannic oxide, the flameproofing properties of which were discovered and patented by Perkin (*8*). In fact, they question the effectiveness of stannic oxide, stating (*9*): "Although hydrated stannic oxide is usually regarded as a permanent fireproofer, fabric with 40 percent of this substance was found to burn readily after a short exposure to rain."

Ramsbottom and Snoad (*9*) found that fabric treated with stannic oxide precipitated with ammonium sulphate and exposed under glass to sunlight lost 82 percent of its strength, or more, in 6 months, while pieces of treated fabrics stored dry in the dark retained their full strength.

Jarrell and Holman (*5*) found that iron oxide pigments protected cotton duck exposed to sunlight against the extremely destructive action of such waterproofing agents as linseed oil, paraffin, and petrolatum.

Explanations of the several types of fireproofing action have been advanced. Gay-Lussac (*4*) found that a fireproofing substance may prevent burning either by forming an incombustible melt over the surface or by yielding noncombustible gases which prevent ignition of combustible gaseous evolution products. Ramsbottom and Snoad (*9*) suggested that "endothermic changes" may take place in the fireproofing agent itself, causing the flame to be extinguished, or that the heat of combustion may be conducted away so rapidly by the fireproofing agent that the temperature of the material is kept below the ignition point. They concluded that only the easily reducible oxides are flameproofing agents, but did not attempt to explain why.

So far as is known, no one has yet satisfactorily explained the flameproofing action of stannic oxide.

EXPERIMENTAL WORK

In the preliminary work in the Bureau, in which the dry oxides were mixed mechanically with fabric which had been pulped by grinding in a utility mill, manganese dioxide, cupric oxide, and a 30:55:15 mixture of cupric oxide, manganese dioxide, and cobalt oxide rendered the fabric flameproof, while titanium dioxide and aluminum oxide did not. These results are in harmony with Ramsbottom and Snoad's findings that only the easily reducible oxides are flameproofing, but are not in agreement with those of Lochtin (*7*) that aluminum hydroxide precipitated by a carbonate is satisfactory as a fireproofing agent. Aluminum hydroxide precipitated by a carbonate, the excess carbonate and bicarbonate being washed out, has not been found a satisfactory fireproofing agent. Any fireproofing qualities apparently possessed by it are readily attributable to the alkali carbonates and bicarbonates, which it retains tenaciously.

Perkin and other investigators of the flameproofing effect of stannic oxide deposited the oxide from sodium stannate solution by means of a solution of ammonium sulphate. With this procedure, provided the ammonium and sodium sulphates, hydroxides, and carbonates are thoroughly leached out (it is very doubtful if this can be done completely), only hydrated stannic oxide remains in the fabric. In the course of the work described in this circular, solutions of copper sulphate, manganese sulphate, chromium sulphate, titanium sulphate, ferric sulphate, and sulphuric acid were used in fixing stannic oxide in the fabric. These were all tried in order to determine whether other precipitants would increase the effectiveness of stannic oxide over that obtained by ammonium sulphate precipitation. An increase in the effectiveness of stannic oxide would obviously reduce the amount necessary to impart a given degree of flame resistance. This is desirable because of the high cost of tin and its compounds.

In the experiments in which metal sulphates were used to precipitate stannic oxide, an undetermined but small quantity of the hydrated oxide of the metal in the precipitant was also deposited on the fabrics. Sulphuric acid in slight excess appeared to be as effective in precipitating the stannic oxide as the metallic salts, and little difference in the resistance of the treated fabrics to flaming could be observed, although it was noted that all of them showed less tendency to flame than when ammonium sulphate was used as the precipitant. In all cases, the excess precipitant was well leached out before the fabrics were tested for flame resistance. It was found during this work that squeezing and drying the fabric at certain stages, strongly emphasized by Perkin (*8*), was unnecessary. Therefore, in the work described in this circular, after saturating the fabric with sodium stannate solution, it was allowed to drain and then dried without squeezing out the excess solution. The dried fabric was then immersed in the selected heavy metal salt solution for a short time to precipitate the stannic oxide, washed in flowing water to remove the soluble salts, and finally dried. The flame resistance was then determined.

Since the determination of resistance to flaming is a matter of judgment rather than of measurement, a procedure and a standard to serve as a basis in judging resistance were obtained by impregnating pieces of cotton duck with sodium stannate solution, a solution of different strength being used for each. The stannic oxide was precipitated in each piece with an ammonium sulphate solution of the same strength, leached to remove sodium and ammonium salts, and dried. That piece of treated duck which contained so little stannic oxide that when it was held vertically and ignited at an upper corner the flame traveled slowly but steadily across the top was selected as the standard by which to judge the comparative flame resistance of the pieces of duck treated with the other metallic sulphate solutions.

Strips of fabric were impregnated in a similar manner with the dilute solution of sodium stannate with which the above-mentioned standard had been impregnated, and dried. One piece was then put into a 20-percent solution of ammonium sulphate and the other into a 20-percent solution of ferric sulphate. In each case the concentration of the precipitating solution was greater than required to pre-

cipitate the sodium stannate present in the fabric. Immediately after the precipitation of stannic oxide by these solutions, the samples were placed in flowing water and leached to remove the soluble salts remaining in the fabric. The fabric in which the stannic oxide was precipitated by the ferric sulphate was colored a very light buff shade by the precipitated ferric oxide, while the sample treated with the ammonium sulphate solution was, of course, colorless.

The strip in which sodium stannate was precipitated by ferric sulphate did not continue to flame in a horizontal direction, whereas in the strip treated with the same stannate solution and ammonium sulphate, the flame persisted and traveled horizontally the full width of the strip. Results similar to those obtained with ferric sulphate were obtained with the other heavy metal salt solutions mentioned above.

These experiments were repeated until the author was satisfied that the process he had developed would yield a weather-resistant flameproof fabric, the useful life of which would not be materially shortened by the presence of the flameproofing agents, but which would not prevent destruction of the fabric by glowing or flameless combustion. This was accomplished with a stannic and iron oxide content of approximately 18 to 20 percent. Such treated fabric remained flameproof after 6 months' continuous exposure to weather.

Only ferric sulphate was used in the subsequent industrial application of this process for fixing stannic oxide on the fabric, because in the pilot-scale experiments it was found to be the cheapest effective precipitating agent which furnished a protective coloration to the fabric.

FLAMELESS COMBUSTION

The fact that fabric flameproofed by stannic oxide supports a persistent flameless combustion or glowing makes absolutely necessary a supplemental treatment that will inhibit this. Aside from the fact that stannic oxide accelerates the deterioration of fabric exposed to light, its use has probably been avoided because of this persistent glow, which offers in many cases as much hazard as a free flame. Flameless combustion of fabrics treated with stannic oxide is started very easily; in fact, the flameproofed fabric can be set aglow more easily than the untreated fabric can be ignited. In the course of this work, it was found that flameproofed fabric glowed spontaneously when exposed to a current of air the temperature of which was approximately 100° C. below the temperature at which the untreated fabric spontaneously burned.

PROPERTIES REQUIRED IN A SUPPLEMENTAL GLOWPROOFING AGENT

The use of a water-insoluble supplementary agent in conjunction with stannic oxide was patented first by Snyder (*10*) in 1932. Snyder's agent was polymerized vinyl chloride, a resinous substance which decomposes between 200° and 300° C. with evolution of hydrogen chloride. The action of vinyl chloride somewhat resembles that of the water-soluble ammonium salts in that it produces its effect by evolving a flame-extinguishing gas, the most effective of all fireproofing mechanisms when the evolution occurs in the proper manner.

However, there are important and vital differences between chlorinated resins, such as polymerized vinyl chloride, and ammonium salts. Some ammonium salts give off their flame-preventing gases even below 100° C., but are fairly stable at ordinary temperatures. In the second place, the gases evolved by these salts are alkaline and do not injure cellulosic materials, although the acidic residue resulting from loss of ammonia does injure the fabric and eventually destroys its usefulness. The gas evolved by the chlorinated resins, on the other hand, is highly acidic and therefore destructive to cellulose fabrics. An acceptable chlorinated resin must be so stable that no decomposition whatever occurs at ordinary temperatures.

Since effective fireproofing agents must exert their action at relatively low temperatures, it follows that a chlorinated resin which gives off flame-preventing gases only in the higher temperature ranges will not be fully effective. The decomopsition range of commercial chlorinated resins available during this work was so high that the evolution of hydrogen chloride was not sufficient to prevent combustion of the fabrics. On the contrary, ammonium salts decompose at temperatures that make them completely effective when used alone.

The chlorine content of a chlorinated resin is not always a direct measure of its fireproofing effectiveness. The temperature and the rate at which hydrogen chloride is evolved play a major part in determining the effectiveness of any given resin. Probably other factors are involved. For example, chlorinated rubber, which contains a very high percentage of chlorine, has relatively little fireproofing value in spite of the fact that chlorinated rubber films in themselves burn with difficulty. A probable explanation of this low fireproofing value lies in the high viscosity of chlorinated rubber solutions. It appears that penetration of the cellulosic or other combustible material by the fireproofing agent is necessary. The high viscosity and low wetting power of chlorinated rubber solutions permit only an impregnation of the outer surface of the fabric. It seems safe to say, therefore, that wetting and penetrating power indirectly affect the fireproofing effectiveness of a chlorinated resin.

By way of summation, the properties to be sought in developing a resin specifically for fireproofing purposes are (1) sufficient instability to permit heavy evolution of hydrogen chloride well below the temperature of exothermic thermal decomposition of cellulose, which from Chorley and Ramsay's results (*3*) appears to be between 300° and 325° C., while at the same time remaining entirely stable at all temperatures to which fabrics are exposed in ordinary use. (2) The resin should be stable to light of all wave lengths to which the fabric will be exposed. It is doubtful whether this property can be attained. (3) It should be sufficiently soft and fluid to preserve the softness and flexibility of the fabric without undue use of plasticizers. (4) It should have low volatility. (5) It should be essentially colorless in order not to affect the color of fabrics. (6) The physical properties should be changed very little by temperature. Finally, the cost should be low.

Even a fully effective fireproofing material which acts by evolving flame-preventing gases does not prevent the evolution of combustible gases when the fabric is heated. Such a fireproofing material

exerts its fireproofing action in two ways. The incombustible gases which it evolves exerts a smothering action by lessening the supply of oxygen, and in addition they raise the ignition temperature of the combustible gases. The evolution of combustible gases from cellulose becomes exothermic and spontaneous in the neighborhood of 300° C., and it has been observed that all effective fireproofing agents of the flame-smothering type evolve the flame-smothering gases well below this temperature. Flame propagation results from the heating effect of burning portions upon adjacent unignited areas, causing the evolution of combustible gases from these areas. If the area adjacent to a flaming area has been impregnated with a substance which decomposes and liberates a flame-extinguishing gas before the temperature of the adjacent area reaches the point at which ignitible gases are given off exothermically, not only will flame not spread, but it (the flaming portion) will be extinguished as soon as the igniting cause is removed.

Up to the present, so far as is known, no chlorinated resins have been developed which impart fireproofness when used alone. Therefore, their present field of usefulness lies in their use with stannic oxide or other flameproofing agents to inhibit flameless combustion and to supplement the flameproofing action of such agents. In this capacity the chlorinated resins serve a useful function, and can be used to replace partially the more costly tin oxide.

PREPARATION OF A FIREPROOFING RESIN

Before a satisfactory weather-resistant fireproofing treatment for cotton fabrics could be developed, a more suitable chlorinated resin was needed. The commercially available resins were not designed for use in fabrics, and could be used only when combined with a high percentage of plasticizer or softening agent. Moreover, the resins available could not be widely used in fireproofing because of their cost. For these reasons, the development of a more suitable resin was attempted.

After some experimentation, it was found that chlorination of mixtures of paraffin wax and so-called paraffin-base petroleum oils yielded soft resins, the softness of which varied with the melting point and percentage of wax in the initial mixture. The chief objection to the use of petroleum derivatives as sources of raw materials is that the nature and composition of these materials, even when obtained from the same producer, may vary from time to time. This objection is not insurmountable, because considerable latitude is allowable in the final chlorinated product. However, one brand of wax was found which gave entirely unsatisfactory results.

Impurities also played an important part in determining the characteristics of the end product. For this reason, it was found necessary to carry out the chlorination in apparatus constructed entirely of glass or other nonmetallic material. The raw materials were dissolved in carbon tetrachloride in sufficient volume to prevent too great an increase in viscosity as the chlorination proceeded. The proportions of materials found satisfactory were one part (by weight) of paraffin wax melting at 50° or 55° C.; one part of oil having a viscosity of 74 seconds Saybolt at 37.8°; and five parts of

carbon tetrachloride. Usually it was necessary to add more carbon tetrachloride before the chlorination was complete. Refluxing was not employed.

The apparatus used in the pilot-scale preparation of the chlorinated resin was an exact but greatly enlarged duplicate of the laboratory apparatus, and consisted of a battery of vertical pyrex glass cylinders sealed at the bottoms and equipped with two-hole rubber stoppers at the tops. The cylinders were 6 inches in internal diameter and 6 feet high. They were loosely packed with glass wool, which served as a baffle for the ascending chlorine gas and also as a contact catalyst. The chlorine was led to the bottoms of the cylinders through heavy-walled tubes of ½-inch internal diameter, which were inserted through one hole of each stopper. Each chlorine-supply tube was equipped with a side arm near its upper end outside the cylinder. Through the other hole of each stopper was inserted one leg of a Y-tube, the long axis of which was bent at right angles to facilitate connecting the cylinders. By means of heavy rubber tubing the various cylinders were then connected in such a way as to permit circulation of chlorine either to each cylinder independently (in parallel) or from cylinder to cylinder (in series). The latter procedure was employed when the product neared the saturation point, to prevent excessive loss of chlorine.

Chlorination was continued until a sample of the product, freed of hydrogen chloride, was sufficiently fire-resistant to prevent downward travel of flame in a vertical strip of bleached duck which was fully ignited at the top. Resin to the extent of from 25 to 30 percent of the total impregnated fabric weight was necessary to provide this degree of fire resistance. It was necessary to chlorinate the mixture essentially to saturation (about 60 to 62 percent chlorine content) before the fire resistance was satisfactory.

The chlorination proceeded very rapidly in bright, natural light, and less rapidly in artificial light. The process was sufficiently exothermic in its earlier stages to cause the carbon tetrachloride to boil. No artificial heat was employed in the process, but chlorination would be expedited in the later stages if this were done. The reaction appeared to be accelerated at slightly elevated temperatures, probably indirectly because the lowered viscosity permitted freer circulation of the chlorine through the liquid. Chlorination was continued until the reaction became so feeble that it was apparent little chlorine was being absorbed. Fire resistance of this product increased directly with the degree of chlorination. Consequently, underchlorination rather than overchlorination was the possibility to be avoided.

It was found that if the chlorinating cylinders were connected in series at the beginning of the chlorination, the end product in the first cylinder was much the lightest in color. The first cylinder absorbed all the chlorine, and the passage of the resulting hydrogen chloride from the first cylinder through the subsequent cylinders, prior to absorption of chlorine, permanently darkened the product. This coloration was avoided by passing chlorine in parallel until the chlorine-saturation point was approached.

During the course of the present work, such problems as solvent recovery and continuous recharging of the chlorination apparatus

were not worked out. The recharging could easily be done by withdrawing the contents of the first cylinder by suction, and then putting pressure on the exit end of the system, forcing the contents of each cylinder back into the one next preceding it. The last cylinder would then be recharged with a fresh carbon tetrachloride solution of wax and oil.

When the product from any one cylinder was found sufficiently chlorinated, it was withdrawn and diluted with mineral spirits or any other desired solvent, and air was bubbled through the solution until it was essentially free from dissolved hydrogen chloride and chlorine. The chlorinated product was miscible with acetone, carbon tetrachloride, chloroform, mineral spirits, and other solvents. When a wax melting at 50° C. was used to make the resin, the solvent-free product was soft and sticky and had a light-brown color. When diluted it gave light, straw-colored solutions.

USE OF CHLORINATED RESIN WITH STANNIC OXIDE

The finished solvent-free resin was soft and sticky, and it could be used in fabrics without modification by softeners or plasticizers. In some cases, however, the addition of a softening agent, which in itself exerted no fireproofing action, improved the fireproofing properties of the resin. This may have been due to an increased wetting or penetrating power produced in the resin by the addition of the softener. Tricresyl phosphate, triphenyl phosphate, and chlorinated diphenyls were found satisfactory as softeners. Usually, one part of softener to from three to five parts of resin by weight was the proportion used. Beeswax was sometimes used to increase the water repellancy of the resin.

In applying the resin to a fabric, the concentration of the resin solution was adjusted to permit the fabric to retain enough resin on a solvent-free basis to equal about 27 percent of the total treated weight, including oxides. It was found by repeated trials that approximately this quantity is required to insure satisfactory fire resistance. The take-on varied with the solvent employed and with the machinery used to apply the resin. A petroleum fraction boiling between 150° and 200° C. was found to be a satisfactory solvent from the standpoint of both volatility and cost.

The resin produced as herein described had a very high wetting power, and one rapid passage of the fabric through the resin solution sufficed to impregnate it thoroughly. The fabric was treated with the resin after it had been treated with stannic oxide.

It was found by the author that all resins which possess fireproofing properties, including those developed during this work, split off hydrogen chloride rather freely upon exposure to direct sunlight. It was further found that the splitting off of hydrogen chloride is inhibited in somewhat varying degrees by the presence of oxide pigments of any color other than white. For this reason, chlorinated resin must be used in combination with protective pigments, and this precludes its use in white fireproofed fabrics for outdoor purposes.

In order to obtain quantitative information on the effects of the various components of the treatment, fabric samples were treated

in the laboratory and exposed in a nearly horizontal position out of doors at the Arlington Experiment Farm, Rosslyn, Va., from March 6 to September 11, 1934. Tensile-strength tests [3] were made on conditioned samples of identical thread count after exposure. The results are given in table 1.

TABLE 1.—*Tensile strength of treated samples after exposure out of doors near Washington, D. C., from Mar. 6, 1934, to Sept. 11, 1934*

Treatment	Average breaking strength	Ash content of fabric, including oxides	Treatment	Average breaking strength	Ash content of fabric, including oxides
	Kilograms	*Percent*		*Kilograms*	*Percent*
None (unexposed)	39.3	1.0	SnO_2, Fe_2O_3, and resin	17.5	8.37
None (exposed)	24.9	1.0	SnO_2, Cr_2O_3, and Fe_2O_3	24.5	9.95
SnO_2	2.0	7.25	SnO_2, Cr_2O_3, Fe_2O_3, and resin	25.7	9.95
SnO_2 and resin	2.0	7.25	SnO_2 and Cr_2O_3	16.7	6.27
SnO_2 and Fe_2O_3	12.8	8.37	SnO_2, Cr_2O_3, and resin	11.3	6.27

In all the samples containing colored oxides the excess precipitant remaining in the fabric after precipitation of the stannic oxide was in turn precipitated by ammonia, and the treated fabric was then thoroughly washed by leaching. Because of the varying factors involved in the preliminary wetting out and in hand treating the fabric samples, the treatment could not be duplicated exactly in the strips. The ash values are based on the total weight of fabric and oxides before the resin was applied. The deterioration occurring in the check or untreated sample, namely, about 37 percent, agrees fairly well with the results obtained by Jarrell and Holman (*5*) for the rate of deterioration of untreated fabric under like conditions of exposure. The results obtained with stannic oxide when used alone are also in agreement with those of Ramsbottom and Snoad (*9*), namely, that stannic oxide used alone causes almost complete deterioration of exposed fabrics over a 6-month period. These results indicate further that by addition of not more than 2 or 3 percent of mixed oxides of iron and chromium, based on ash determination before application of resin, it is possible at least to offset the destructive action of both stannic oxide and chlorinated resins. Some of the commercial thermoplastic chlorinated resins were also tested, and the effects upon the life of the fabric were found to be comparable with those obtained with the specially developed paraffin resin.

The treated fabric samples in table 1 were all impregnated with sodium stannate solution of the same strength, namely, 10 percent by weight. The resin was softened by the addition of a relatively small percentage of chlorinated diphenyl of the liquid type. The take-up of resin amounted to about 28 percent of the total treated weight.

At this stage of the work it was decided to study this method of treatment on a pilot-scale basis. The laboratory work gave evidence that the treatment should have value, but very little information

[3] A Schopper 100-kg hand-operated tensile-strength machine was used in these tests. The distance between the jaws was $1\frac{1}{16}$ inches, and they opened at an average speed of $1\frac{1}{16}$ inches in 10 seconds.

could be gained in the laboratory as to difficulties which might be experienced in larger scale operation or as to the cost of the treatment. Accordingly, a cooperative agreement was entered into between the Department of Agriculture and a commercial textile-converting firm.

COOPERATIVE INDUSTRIAL INVESTIGATIONS

After extended impregnation experiments on a semiplant scale, it was decided to employ a concentration of 1 pound of an acceptable grade of commercial sodium stannate per gallon of water, and for each 10 pounds of stannate, 1 pound of fresh caustic soda was added to the solution. The caustic soda is necessary to prevent hydrolysis where stannate solutions are to be kept for any length of time, as otherwise there is a tendency for the dissolved stannate to decompose, with liberation of an insoluble compound of tin.

When unbleached canvas is being impregnated it is necessary first to wet out the fabric with a suitable wetting agent. A 0.2-percent hot solution of a commercial wetting agent consisting essentially of sodium lauryl sulphate was found to be satisfactory for this purpose. There was an indication, however, that the presence of the wetting agent in the fabric interfered with the precipitation of stannic oxide. Consequently, the fabric was washed well in water after wetting, and after being squeezed to remove as much water as possible, was passed through the hot stannate solution. No attempt was made to maintain the concentration of the sodium stannate solution, as would have to be done during continuous large-scale operation.

The impregnating machinery used comprised six box compartments, each with four rollers at the top and four at the bottom. In passing through each compartment the fabric traveled a distance of approximately 27 feet at a speed of 25 feet per minute. Passing in and out of the treating solution four times in each compartment helped to impregnate the fabric. The compartments held 400 gallons, but only the washing compartments were full during operation. The first compartment contained 100 gallons of wetting solution, the second and third compartments were filled with water, the fourth contained 100 gallons of hot stannate solution, and the fifth and sixth contained 55 gallons each of hot stannate solution. The fabric passed between rollers before entering each compartment and upon leaving the last compartment. The final squeezing was only moderate. The fabric was then passed over steam-heated drying drums, care being taken to keep the steam pressure low, especially during the final stages of drying. Too high a temperature when the stannate impregnated fabric is almost or entirely dry may result in serious lowering of the tensile strength.

After being dried, the fabric was again passed through the impregnating machinery, the first compartment of which now contained a warm solution of 60 pounds of anhydrous ferric sulphate in 50 gallons of water. The commercially treated fabric appeared to show somewhat less resistance to weather exposure than the laboratory-prepared samples. Better results might have been obtained had the concentration of ferric sulphate been somewhat higher.

The second compartment contained 200 gallons of water to which was added 20 gallons of ammonia of 26° Baumé. This was about the minimum concentration of ammonia which could be used and still give satisfactory precipitation of ferric hydroxide. Greater concentrations of ferric sulphate might require higher concentration of ammonia. It was important that the fabric travel at a uniform rate through the ammonia solution; otherwise it became streaked.

The last four compartments contained water. The byproducts of the stannate and ferric sulphate precipitations are sodium and ammonium sulphate. The former is not objectionable, but ammonium sulphate exerts a destructive effect upon cotton fabrics over extended periods in storage, and it is therefore desirable that the soluble salts be washed out. From the final washing compartment the fabric passed between rollers and was then dried as before.

Ferric sulphate solutions have an extremely corrosive action on iron equipment, largely because of their oxidizing nature. It should be feasible to utilize the less corrosive ferrous iron salts in place of a ferric salt. Ferric sulphate was used chiefly because it is easily handled and dissolves readily. The anhydrous form is now available, and this form makes it easy to duplicate concentrations exactly.

When the oxide impregnation was completed, the fabric possessed a pleasing light-brown shade. It yielded an ash of about 12.4 percent based on total weight. Not more than 5 or 6 percent of the total treated weight was stannic oxide. The ash of the fabric was 1 percent, and, therefore, somewhat less than half the increase in weight was due to ferric oxide. The fabric possessed considerable flame resistance, as shown by the fact that when a strip 12 inches long and 2 inches wide was suspended vertically and the lower end ignited for 10 seconds with a Bunsen burner flame, the flaming persisted with difficulty when the burner was removed. It was not desired to render the fabric completely flameproof, since the chlorinated resin was depended upon to complete the flameproofing process in addition to rendering the fabric glowproof.

Measurement of the flame-resistant properties of oxide-treated fabric must necessarily be subject to considerable latitude. It may be stated with reasonable accuracy, however, that this fabric, containing not more than 6 percent of stannic oxide precipitated by ferric sulphate and also containing approximately 6 percent of ferric oxide, displayed as much flame resistance as fabric containing as much as 10 percent of stannic oxide precipitated by the Perkin method. Since under present market conditions stannic oxide is approximately 20 times as expensive as ferric oxide, the partial replacement of stannic oxide is of economic importance.

The flame resistance of fabric samples at each of the stages of treatment is shown graphically in figure 1. The treated samples were taken from experimental mill-scale runs.

THE MECHANISM OF FLAMEPROOFING

In this investigation the practical aspects of the research on fireproofing were stressed rather than the theoretical aspects. Close observation, however, supplemented by preliminary quantitative tests, established certain facts which appear to indicate that the action

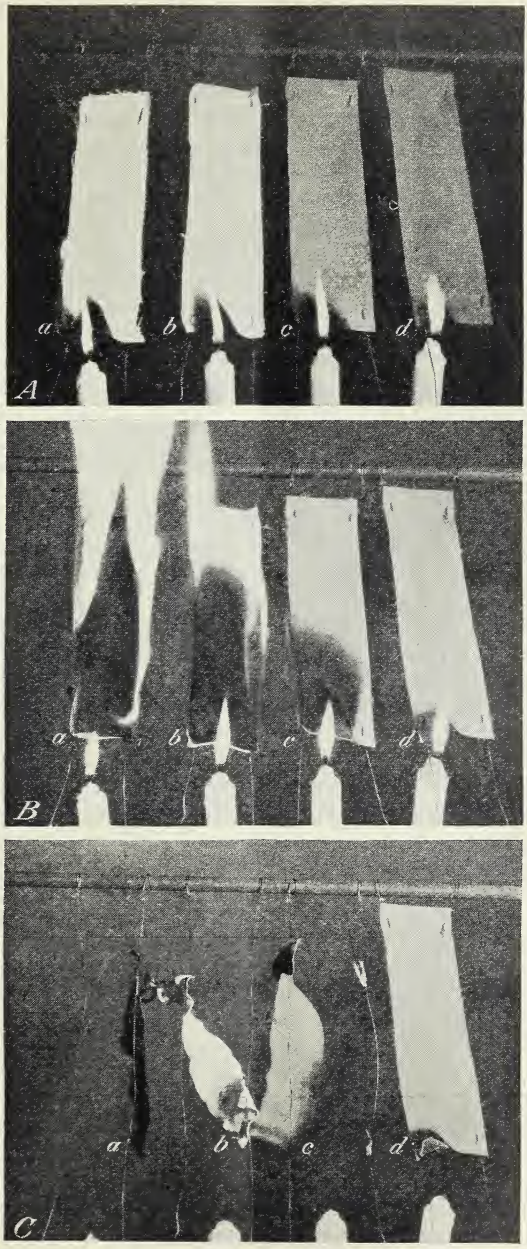

FIGURE 1.—Flame resistance of cotton duck treated in different ways. *A*, 20 seconds after strips were ignited; *B*, 25 seconds after strips were ignited; *C*, 90 seconds after strips were ignited. *a*, Untreated; *b*, treated with 10 percent sodium stannate solution and precipitated with ammonium sulphate solution, washed and dried; *c*, treated with 10-percent sodium stannate solution and precipitated with ferric sulphate, washed, and dried; *d*, treated with 10-percent sodium stannate solution and precipitated with ferric sulphate, washed, dried, and impregnated with chlorinated resin.

of stannic oxide in preventing flaming is catalytic. This action increases the proportion of carbon dioxide and water vapor in the evolved gases to a point which is sufficient to prevent flaming.

Fabrics into which 18 percent or more of stannic oxide has been precipitated and soluble salts washed out cannot be made to flame after the igniting source has been removed, showing either that no combustible gases are produced in the presence of stannic oxide or that combustible gases are so diluted by noncombustible volatile products that they will not flame.

Untreated fabric from which the flame has been extinguished glows but a relatively short time, leaving a black, carbon-containing ash. As long as it glows, much visible pungent smoke is evolved.

Fabric containing sufficient precipitated stannic oxide continues to glow until the fabric has been entirely consumed and a white, practically carbon-free ash remains. Kramer (*6*) has shown that many oxides facilitate the combustion of carbon through catalytic action and that under the influence of such oxides carbon begins to burn at much lower temperatures than when no oxide is present. It seems probable therefore that the afterglow is the result of catalytic incandescent oxidation of carbon following catalytic pyrogenic decomposition of the cellulose. There is less visible smoke from treated than from untreated fabrics during the glowing period, although the glowing treated fabrics also give off a pungent odor.

When equal weights of fabric samples, treated and untreated, were heated in a combustion tube in a stream of carbon dioxide-free air for 15 minutes at 300° C. and then for 45 minutes longer while the temperature was gradually increased to 500° to oxidize all carbon, approximately 60 percent more carbon dioxide was obtained from the treated than from the untreated samples. After carbon dioxide was absorbed from the collected gases, the remaining gaseous combustible matter was burned by numerous passages over an incandescent platinum coil. The volume of carbon dioxide found after this combustion was about the same for the treated as for the untreated samples. The combustible gases collected from the treated samples contained no detectable amounts of carbon monoxide, and the combustible gases from the untreated samples contained a variable volume, in no case exceeding 106 cc from an 0.8-g sample. The carbon monoxide analyses were made with the apparatus designed by Bone and Wheeler (*2*).

In another experiment equal weights of treated and untreated samples were placed in specially designed glass containers and heated for 180 seconds at 325° C. in a molten metal bath. The flameproofed samples, which contained 16 percent of stannic oxide, gave off distinctly larger quantities of water and showed visibly greater darkening of color, obviously due to the more rapid charring and setting free of larger quantities of carbon. In this experiment the samples were free from moisture, and precautions were taken to exclude atmospheric moisture during the experiment. Dried nitrogen was flushed through the containers both before and after heating until equilibrium was established in each case. Under the conditions of this experiment approximately twice as much water was evolved from the treated samples as from the untreated samples.

That more charring occurred and more carbon was set free in the treated fabric was clearly indicated by the following experiment. Treated and untreated samples were heated at 325° C. in a stream of oxygen-free nitrogen in a combustion furnace for 2 hours. At the end of 2 hours, an absorption train was connected to the combustion tube, and the destructive distillation residue was burned in a stream of oxygen. The amount of carbon in the residue was determined from the carbon dioxide collected. The original weight of cellulose in the sample, corrected for ash and moisture, was known, and the carbon in the sample was calculated from the empirical formula for cellulose. The percentage of original carbon in the residue was also calculated. In the treated samples approximately 54 percent of the carbon in the original cellulose remained in the carbonized residue; in the untreated samples only about 32 percent remained behind. Apparently, in the untreated fabric samples about 68 percent of the carbon was evolved in the form of volatile compounds during destructive distillation in nitrogen, whereas in the treated samples only about 46 percent was so evolved.

Since the action of stannic oxide in flameproofing fabrics appears to be of a catalytic nature, an explanation may now be offered of the increased flameproofing effect of stannic oxide when precipitated from sodium stannate solutions by heavy metal salts. Like ammonium salts, such salts are acidic in solution because of hydrolysis, but in the presence of the alkali which is characteristic of sodium stannate, ammonium salts liberate alkaline ammonia, whereas heavy metal salts do not. With the heavy metal salt precipitation, less alkali should be adsorbed by the stannic oxide, which precipitates in the fabric in the form of a hydrated gel. Whitesell and Frazer (*11*) found that when manganese dioxide was prepared free of adsorbed alkali, its catalytic activity in the oxidation of carbon monoxide was greatly increased. Van Bemmelen (*1*) found that manganese dioxide, stannic oxide, and silicon dioxide actually adsorbed alkali from alkali sulphate, with a liberation of sulphuric acid. He used potassium sulphate in his work.

In view of the fact that earlier workers have shown that alkali is strongly adsorbed by catalytically active hydrated oxides and that alkali is definitely a catalyst poison, there is reason to assume that the increased flameproofing effect obtained when sodium stannate is precipitated by heavy metal salts may be due to at least a partial removal of the poisoning alkali from the precipitated stannic oxide.

Reference has been made to the deteriorating effect of stannic oxide on cotton fabrics exposed to sunlight (p. 10). On first thought, no similarity would appear to exist between the thermally induced breakdown of cellulose into carbon, carbon dioxide, and water by hydrated stannic oxide and the disintegration of treated fabric upon exposure to sunlight. After exposure to sunlight for a sufficient time, disintegration reduces the fabric to a condition in which it can be pulverized between the fingers. This disintegrating process does not occur to a noticeable extent in the dark. It may be assumed, therefore, that the action exerted by stannic oxide is induced by certain actinic rays, which are known to exert an activating influence upon many different types of reactions. It is well known that a catalyst

for a certain reaction is also a catalyst for the reverse reaction. Therefore, since there seems to be good evidence that stannic oxide induces the more rapid and more extensive break-down of cellulose to carbon, water, and unidentified products at the comparatively low temperature of 300° to 325° C., it seems reasonable to postulate that when properly activated, stannic oxide also induces the hydration, hydrolysis, or oxidation of cellulose at ordinary temperatures. This hypothesis offers one explanation for the more rapid disintegration of stannic oxide-treated fabric in sunlight.

The processes occurring during exposure to direct sunlight do not cause any darkening of the fabric, and the fully disintegrated fabric is as colorless as the freshly treated fabric. Obviously, therefore, it is not the setting free of the carbon of the fabric which causes the disintegration. It is highly improbable that dehydration could be continued to the point where the fabric loses all its tensile strength without separation of some carbon. On the other hand, hydrolysis of cellulose to hydrocellulose or oxidation to oxycellulose would occur without separation of carbon or any visible change in the appearance of the fabric.

The data appear to indicate that the flameproofing action of stannic oxide is due to its catalytic pyrogenic decomposition of cellulose, during which the proportion of carbon dioxide and water resulting from the oxidation of cellulose is sufficient to dilute the volatile and inflammable destructive distillation products so that they cannot burn. This initial stage is followed by the stage of catalytic incandescent surface combustion in which the carbon set free in the first stage is completely oxidized, probably with some temporary intermediate reduction of stannic to stannous oxide, leaving a white ash composed largely of stannic oxide.

SUMMARY AND CONCLUSIONS

The terms "fireproof" and "flameproof" are defined, and the more pertinent literature on fireproofing is briefly reviewed. The precipitation of stannic oxide is discussed in some detail in explaining the greater flameproofing effectiveness of stannic oxide which results when the Perkin method of precipitation is modified by substituting a heavy metal salt for ammonium sulphate.

The destructive action of stannic oxide on fabric during exposure to sunlight, which was demonstrated by Ramsbottom and Snoad, is shown to be largely inhibited by the presence of colored metallic oxides.

The properties desired in a fireproofing resin are pointed out. The preparation and use of a new chlorinated resin are discussed. This resin evolves hydrogen chloride at the combustion temperature of cellulose, which prevents the afterglow induced by stannic oxide. The resin acts as a supplementary fireproofing agent. The part played by the chlorinated resin is compared with the fireproofing action of the ammonium salts, and the limitations of the chlorinated resin are explained on the basis of the decomposition temperatures of the two materials.

The chlorination method is briefly described with respect to raw material, apparatus, and control of the chlorinating process. The

use and function of plasticizers are discussed, and the method of applying the resin to fabric is described.

The treated fabric was completely fireproof after 6 months' exposure to the weather. Exposure tests showed, however, that in all combinations tried the preservative effect of the combined oxide-resin treatment does not lengthen the life of the fabric.

The cooperative commercial development of the fireproofing process is outlined, and it is shown that the process worked out is technically suitable for industrial application.

A theory for the flameproofing action of stannic oxide is suggested. The poisoning action of adsorbed alkali on catalytic activity is discussed, and the increased flameproofing effect of stannic oxide as the result of precipitating sodium stannate in an acidic environment is considered from this angle.

Evidence is submitted that indicates the flameproofing action of stannic oxide may arise from a thermal catalytic decomposition of cellulose in which stannic oxide acts as the catalyst.

LITERATURE CITED

(1) Bemmelen, J. M. van.
1881. die verbindungen einiger fester dioxydhydrate mit säuren, salzen und alkalien. Jour. Prakt. Chem. (N. F.) 23: 324–349.

(2) Bone, W. A., and Wheeler, R. V.
1908. an accurate form of gas analysis apparatus for commercial and other purposes. Jour. Soc. Chem. Indus. 27: 10–12, illus.

(3) Chorley, J. C., and Ramsay, W.
1892. on the destructive distillation of wood. Jour. Soc. Chem. Indus. 11: 395–403, 872–874, illus.

(4) Gay-Lussac [J. L.]
1821. note sur la propriété qu'ont les matières salines de rendre les tissus incombustibles. Ann. Chim. et Phys. (2) 18: 211–216.

(5) Jarrell, T. D., and Holman, H. P.
1923. effects of treating materials and outdoor exposure upon water resistance and tensile strength of cotton duck. Indus. and Engin. Chem. 15: 607–610.

(6) Kramer, W. A.
1927. the catalytic oxidation of carbon. Thesis, Ph. D., Ohio State Univ.

(7) Lochtin, P.
1893. ueber flammenschutzmittel. Dinglers Polytech, Jour. Jahrg. 74 (bd. 290): 230–235.

(8) Perkin, W. H.
1912. the permanent fireproofing of cotton goods. 8th Internatl. Cong. Appl. Chem., Washington and New York, 28: 119–134.

(9) Ramsbottom, J. E., and Snoad, A. W.
1930. the fireproofing of fabrics. Gt. Brit. Dept. Sci. and Indus. Research, Fabrics Co-ordinating Research Com. Rpt. 2: 16–94, illus.

(10) Snyder, C.
1932. process of flame-proofing and product formed thereby. U. S. Patent 1,885,870. U. S. Patent Office, Off. Gaz. 424: 226.

(11) Whitesell, W. A., and Frazer, J. C. W.
1923. manganese dioxide in the catalytic oxidation of carbon monoxide. Jour. Amer. Chem. Soc. 45: 2841–2851, illus.

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U. S. GOVERNMENT PRINTING OFFICE: 1938

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